Senior Thesis

NORMALLY ZONED OLIVINES FROM SANTORINI, GREECE: EVIDENCE FOR MAGMA MIXING

Presented in Partial Fulfillment of the Requirements for the Degree of Bachelor of Science in the department of Geological Sciences

by
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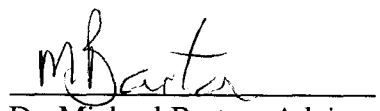

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Introduction

Destructive plate-margin magmas are derived from mantle sources that are mixtures of asthenosphere and subducted oceanic lithosphere (Wilson, 1989). Certain geochemical characteristics of these magmas, such as enrichment in large-ion lithophile elements (LILE) relative to high-field strength elements (HFSE), are believed to reflect mantle source region composition and/or mineralogy. In detail, however, it is difficult to relate the geochemistry of destructive plate-margin magmas directly to source region composition and hence to crustal recycling processes because few, if any, of these magmas represent primary, mantle-derived melts. The compositions of most destructive plate-margin magmas have been altered *en route* to the surface by processes such as fractional crystallization, mixing and assimilation (eg. Leeman and Hawkesworth, 1986; Grove et al. 1988; Hildreth and Moorbath, 1988; Davidson et al. 1990). Clearly, the question is the extent to which the geochemical characteristics of destructive plate margin magmas are inherited from the upper mantle source region or are acquired during ascent through the crust. To address this question, it is necessary to quantitatively evaluate the processes that occur during magma evolution.

The chemical compositions of minerals precipitated from magmas provide a record of the conditions that prevail during magma ascent. Detailed studies of the

zoning patterns in minerals can provide information about the cooling histories of magmas and in many instances provide evidence for magma mixing (Barton et al, 1982). In some cases, studies of zoning have been used to identify xenocrysts that clearly were not in equilibrium with the host melt and that were sampled from the mantle or crust by the magma *en route* to the surface. Such xenocrysts therefore provide information about the mantle source region of the magmas or about crustal material that interacted with the magmas (Barton and Wyers, 1991). Finally, some zoned minerals represent xenocrysts that crystallized from the host magma at high pressure, and they provide information about the evolutionary history of magmas near the base of the crust (Wyers and Barton, 1989).

The research described in this thesis is a study of normally zoned, high magnesium olivines from the Skaros volcano, Santorini, Greece (Fig. 1). Santorini is located in the Hellenic arc. Magmas along this arc have erupted through continental crust that ranges in thickness from 20 to 40 km. Previous workers have shown that Hellenic arc magmas, especially those erupted on Santorini, evolved via fractional crystallization, magma mixing and assimilation in intracrustal magma chambers located at fairly shallow depths (Huijsmans et al, 1988; Huijsmans and Barton, 1989; Wyers and Barton, 1989).

Some magmas erupted from the Skaros volcano on Santorini are unusual in that they contain olivines with highly forsteritic (Fo_{91}) cores. Huijsmans and Barton

(1989) interpreted these cores to represent xenocrysts derived from the upper mantle. A detailed study of these olivines was undertaken in this study.

Geodynamical setting

The tectonic history of the Aegean began with the splitting of Apulia from Africa around 180-200 my BP. Collision between Africa and Eurasia at approximately 45-50 my BP caused Apulia to divide into the Anatolian and Aegean microplates (Barton, personal communication, 1999). The Aegean thus lies between the Eurasian plate to the north and the African plate to the south, and is a region of intense seismic activity with boundaries well defined by the epicenters of shallow earthquakes (Huijsmans, 1985). The southern boundary is formed by the Hellenic trench system, which is up to 5,100 meters deep.

Intermediate and deep focus earthquakes indicate that subduction of the oceanic part of the African plate has occurred along the Hellenic trench system. The initial dip of the slab near the trench system is shallow but the dip steepens to 32-35 degrees to the north (Barton, personal communication, 1999). The slab penetrates to a depth of at least 600 km (Barton, personal communication,1999). The Pliocene-recent Hellenic volcanic arc parallels the trench system where the subducted slab reaches depths of roughly 130-150 km.

The oldest volcanism along the Hellenic arc occurred on Aegina about 4.4 Ma and the most recent volcanic activity occurred on Santorini in 1950 (Huijsmans, et al., 1988) However, most of the volcanic activity occurred about 3 Ma.

Geology of Santorini

Santorini is located near the center of the Hellenic arc about 190 km north of the trench system. Santorini is a volcanic field built by eight eruption centers (Akrotiri, Thera, Megalovouno, Mikro Profitis Ilias, Skaros, Cape Colombos, Palea Kameni, and Nea Kameni) (Fig. 2). A flooded caldera complex was created by at least three collapse events associated with explosive pyroclastic eruptions dated at 100,000 yr, 37,000 yr, and 3,600 yr. The walls of the caldera complex permit stratigraphic relations within individual eruptive centers as well as the temporal relations between the centers to be studied in detail.

Skaros, is a shield volcano located in the northern part of Santorini. Lavas from this volcano erupted into a long-lived depression between lavas erupted by Micro Profitis Ilias and pyroclastics erupted by the Thera volcano (Fig. 2). The lavas erupted by Skaros must be younger than the pyroclastics that are exposed beneath Phira (<37,000 yr), and older than the rhyodacites exposed around the Caldera rim (>18,000 yr).

Lavas erupted by Skaros range in composition from basalt to rhyodacite. Chemostratigraphic studies by Huijsmans and Barton (1989) show that the lavas exhibit cyclic variations in composition. Each of the four eruptive cycles on Skaros began with eruption of Silica-rich magma and ended with eruption of Silica-poor magma. These cyclic variations were interpreted as reflecting simultaneous operation of fractional crystallization and mixing in the sub-volcanic magma chambers prior to eruption. Cribb and Barton (1996) showed that isotopic data require that fractional crystallization and mixing were accompanied by relatively minor assimilation of crustal material during evolution of the Skaros magmas.

Mineral chemical studies by Huijsmans (1985) provide the key evidence that mixing was important during evolution of the Skaros magmas. Mineral chemical data have also been used by Barton (personal communication, 1999) to obtain quantitative estimates of the pressure of crystallization, and hence of depth to the magma chamber beneath Skaros. This work indicates that phenocrysts (olivine, pyroxene, plagioclase, Fe-Ti oxide) in Skaros basalts crystallized at pressures of 0.2-0.3 GPa, so that the magmas were erupted from a chamber located at a depth of ~7-10 km. However, Huijsmans (op. cit) found that the cores of olivines in some lavas are unusually forsteritic (~Fo_{90}), and suggested that these olivines crystallized at high pressure, perhaps in chambers located near the base of the crust (~20 km). One lava containing olivines with highly forsteritic cores (SI 173) was selected for

detailed study to further test this hypothesis.

Petrography

SI173 is a **basaltic andesite** from near the base of the volcano and near the top of the lowermost eruptive cycle. It is **porphyritic** with **phenocrysts of olivine, clinopyroxene, orthopyroxene and plagioclase**.

Olivine forms euhedral to subhedral phenocrysts (up to 1mm, but mostly less than 0.7 mm), and also forms smaller (0.3mm), rounded grains in the groundmass. Some grains form glomeroaggregates with pyroxene. Olivines show normal zoning. Rare grains are rounded with irregular, embayed and resorbed edges. These anhedral olivines contain inclusions of Cr-spinel and represent xenocrysts.

Clinopyroxene mostly forms euhedral to subhedral phenocrysts, although some grains are rounded and anhedral. Clinopyroxene forms glomeroaggrgates with orthopyroxene and with olivine. The clinopyroxenes are normal zoned.

Orthopyroxene forms rounded, anhedral crystals; and is usually rimmed by olivine or clinopyroxene. Some grains of orthopyroxene contain inclusion of Cr-spinel and may represent xenocrysts.

Plagioclase Feldspar occurs as subhedral to euhedral equant phenocrysts up to 3.5mm in size. Albite twinning is very common, and many crystal show sieve-textures suggesting disequilibrium between the cores of the crystal and the host magma. Plagioclase shows oscillatory zoning.

The phenocrysts are set in a fine-grained, intergranular **groundmass** that contains acicular plagioclase, octahedra of magnetite, anhedral clinopyroxene, and rounded olivine.

Analytical method

Compositional data for olivines in sample SI173 were acquired using the Cameca SX-50 electron microprobe in the MARC facility of the Department of Geological Sciences at the Ohio State University. Operating conditions were 15kV acceleration voltage and 20nA sample current. Point analyses were obtained using a 1 μm size beam with 20 second counting times for each element. Nickel and manganese were calibrated on pure metal standards while all other elements were calibrated using high quality mineral standards. The quality of each analysis was judged from calculated structural formula.

Cores and rims of several olivines in the sample selected for study were analyzed to identify grains with highly forsteritic cores. Compositional profiles

were then obtained from strongly zoned olivine grains. The profiles were made by performing spot analyses in traverses from rim to rim with a spot spacing of 30 μm for a large (~1mm) olivine, and a spot spacing of 15 μm for a smaller (~0.5mm) olivine in SI173.

Results

Microprobe analyses are listed in Appendix. 1. Structural formulae were calculated on a 4-Oxygen basis using standard procedures.

Core and rim analyses of individual olivine grains reveal a compositional range from Fo_{86} to Fo_{66}. The high Fo contents were obtained for the cores of anhedral olivines with irregular, embayed, and resorbed rims. Compositional profiles across two of these olivines are shown in figures 3-10. In figures 3 and 4, Fo content is plotted as a function of distance across the crystals (in μm). The cores of both crystals are very similar in composition (Fo_{87-86}), as are the rims of the crystals (Fo_{76-75}).

Minor elements were also analyzed in the olivines. Al and Ti contents were measured primarily to check for contamination during analysis by pyroxene, feldspar and Fe-Ti oxide, whereas Cr was measured to check for contamination by Cr-spinel. The concentrations of all these elements are

consistently low, indicating that the analyses reflect olivine compositions. Ni, Mn, and Ca were analyzed because these elements substitute for Mg and Fe^{2+} in natural olivines. All of these elements also occur in low concentrations. Data for Mn and Ca (plotted as atoms per formula unit, or afu) show considerable scatter (Figures 5-8) which is expected given the large analytical uncertainties in electron probe microanalysis of elements with low concentrations (<0.011 afu for Mn and <0.009 afu Fo Ca). However, both elements show crude **negative** correlations with Fo because both Mn and Ca substitute primarily for Fe^{2+} in olivine (Deer, Howie and Zussman, 1992). Ni should substitute primarily for Mg in olivine (Deer, Howie and Zussman, 1992) and is therefore expected to show a positive correlation with Fo. Data for Ni also show considerable scatter, but no clear correlation with Fo is observed (Figures 9 and 10). The reason for this is unclear. Ni concentrations (average - 0.005 afu) are similar to those of Mn (average - 0.0065 afu) and Ca (average - 0.005 afu), and it appears that the uncertainty in measured Ni at low concentrations is greater than the uncertainties in measured Mn and Ca at low concentrations. Using counting times longer than 20 seconds for minor elements would help circumvent this problem.

Discussion

Origin of the zoned olivines

The Fo contents of the cores of the crystals studied in detail (Fo_{87-86}) are significantly higher than those obtained by Huijsmans (1985) for the cores of olivine phenocrysts (Fo_{76-74}) in the same lava. The rims of the crystals analyzed in this study have compositions (Fo_{76-75}) similar to the cores olivine phenocrysts analyzed by Huijsmans (1985). This provides overwhelming evidence that the resorbed olivines analyzed in this study represent xenocrysts (see petrography). The resorbed textures and the high Fo contents in the cores of the xenocrysts indicates that the latter initially were not in equilibrium with the host magma. The decrease in Fo content from core to rim indicates that the xenocryst partially reequilibrated with the host magma by diffusive exchange of (primarily) Mg and Fe^{2+}. The identical composition of the cores of olivine phenocrysts in the same lava and the rims of the xenocrysts indicates that the latter reached equilibrium with the host magma.

Xenocrysts in lavas can originate in two ways: **1.** magma mixing and; **2.** interaction between magma and the wall rock during ascent.

Mineral chemical studies generally provide conclusive evidence for the operation of magma mixing (Barton et al. 1982). This is illustrated using data

for clinopyroxenes from Huijsmans (1985) in two basaltic andesites (SI22, SI121) from the volcano Megalo Vouno on Santorini in Figure 11. In both lavas, analyses of pyroxene cores define two compositional populations, and analyses of pyroxene rims and microphenocrysts are intermediate in composition to the two core populations. The pyroxene cores are interpreted to be xenocrysts derived form magmas that mixed prior to eruption. The Mg-rich pyroxene cores represent xenocrysts derived from the less-evolved (mafic) magma involved in the mixing event whereas the Mg-poor pyroxene cores represent xenocrysts derived from the more-evolved (less mafic) magma involved in the mixing event. After mixing, neither pyroxene is in equilibrium with the hybrid magma that must have a composition between the compositions of the end members involved in mixing. Therefore, both Mg-rich and Mg-poor pyroxenes experience resorbtion. With cooling after mixing, the magma precipitates a pyroxene of intermediate composition to the Mg-rich and Mg-poor pyroxene xenocrysts, and this equilibrium composition is represented by the microphenocrysts and rims plotted in Figure 11. The resultant hybrid lava thus contains normally zoned pyroxenes with Mg-rich cores, and reverse zoned pyroxenes with Fe-rich cores.

Pyroxene data for sample SI173 (from Huijsmans, 1985) are also plotted in Figure 11. In this case, the cores of pyroxenes also define two compositional

populations, one Mg-rich and the other richer in Fe, but in the case of SI173 pyroxene rims and microphenocrysts are **not** intermediate in composition to the two pyroxene core populations. Pyroxene data for SI173 are thus clearly different from those for samples SI22 and SI121, and it might be argued that these data do not provide evidence for mixing. However, it is important to recognize that pyroxene compositional data indicate that SI22 and SI121 formed by mixing of two magmas ***both of which contained pyroxene phenocrysts*** prior to the mixing event. Pyroxene data for SI173 can be interpreted in terms of mixing if ***only one of the magmas*** (the less-evolved, or mafic end-member) ***contained pyroxene phenocrysts*** prior to the mixing event. In this case, the Mg-rich pyroxene cores represent xenocrysts derived from the less-evolved (mafic) magma involved in the mixing event. After mixing, this pyroxene is in out of equilibrium with the hybrid magma and undergoes resorbtion. With cooling after mixing, the magma precipitates an equilibrium Mg-poor pyroxene that is represented by the phenocryst cores plotted in Figure 11. The resultant hybrid lava thus contains normally zoned pyroxene ***xenocrysts with Mg-rich cores***, and normally-zoned pyroxene ***phenocrysts with cores that are richer in Fe*** than those in the xenocrysts. Finally, the rims precipitate during eruption.

Although the preceding discussion is based on analysis of pyroxenes, it

applies equally well to the olivines described in this thesis. Accordingly, the Mg-rich olivine cores represent xenocrysts derived from the less-evolved (mafic) magma involved in mixing. After mixing, this olivine is out of equilibrium with the hybrid magma and undergoes resorbtion. With cooling after mixing, the magma precipitates an equilibrium Mg-poor olivine that is represented by phenocryst cores of Fo_{76-74}, and olivine of the same composition precipitates as rims around the xenocryst cores. The resultant hybrid lava thus contains normally zoned olivine ***xenocrysts with Mg-rich cores,*** and normally-zoned olivine ***phenocrysts with cores that are richer in Fe*** than thoses in the xenocrysts. The zoning pattern in the olivines described in this study reflect reequilibration of the olivine xenocrysts with the host magma by diffusive exchange of (primarily) Mg and Fe^{2+}.

The composition of the olivine xenocryst cores (Fo_{87-86}) allows the Mg-rich (mafic) end-member involved in mixing to be identified because Huijsmans (1985) provides analytical data for olivines from a large number of lavas from Santorini. Only one of the lavas analyzed by Huijsmans (op cit.), a basalt from the Akrotiri peninsula (SH32), contains olivine phenocrysts with compositions of Fo_{87-85} that also contain inclusions of Cr-spinel (see section on petrography above). SH 32 also contains Mg-rich pyroxenes, and represents the most primitive magma erupted on Santorini. Basalts found on the Akrotiri

peninsula were some of the earliest magmas erupted on Santorini. As such they represent strong candidates for the primitive or mafic end-members involved in mixing to form hybrid magmas erupted later from other volcanoes such as Skaros. In fact, recent work on temporal variations in volcanic activity in the Santorini volcanic field indicates that abundant basalts only erupted during the initial phase of activity. As activity progressed and intracrustal magma chambers were established, basalts rising from the mantle were intercepted by, and mixed with, evolved magmas in these chambers (Barton, personal communication, 1999). Therefore, the younger lavas and pyroclastics, such as those erupted by the volcano Skaros, represent hybrid or mixed magmas.

Although the occurrence of olivine (and clinopyroxene) xenocrysts in SI173 is adequately explained by the magma mixing hypothesis, it is impossible to rule out the possibility that these xenocrysts represent crystals sampled from the wall rock by the magma during ascent. In fact, distinguishing between xenocrysts that represent accidental inclusions derived from the wall-rock and those derived from magmas involved in mixing is not a simple task. However the importance of mixing has been documented for lavas erupted on Santorini, including those erupted by the Skaros volcano, so that mixing appears to provide the most likely explanation for the occurrence

of olivine xenocrysts in SI173. The following observations support this conclusion.

1. Sieve-textures of the type observed in plagioclase phenocrysts in sample SI173 are widely thought to form as the result of mixing, and are common in other hybrid lavas erupted on Santorini.

2. Quantitative modeling of geochemical variations shown by lavas erupted by Mikro Profitis Ilias (Cribb and Barton, 1996) and by Skaros (Barton, personal communication, 1999) indicate that the primitive end-member involved in mixing to produce hybrid magmas beneath both eruptive centers was a basalt identical in composition to SH32 from the Akrotiri peninsula. As described above, the olivine xenocrysts in SI173 have compositions identical to olivine phenocrysts in basalt SH32, and therefore provide additional evidence that the SH32 represents the mafic end-member involved in mixing. Obviously then, SI173 represents a hybrid formed by mixing between basalt SH32 and an evolved magma in the plumbing system beneath the Skaros volcano.

Residence time of the olivine xenocrysts

The zoning patterns in the olivine xenocrysts reflect diffusive reequilibration between the cores of the crystals and the hybrid magma formed during the mixing event. It is therefore possible to calculate the time for the zoning to develop by solving the appropriate equation for diffusion in a sphere. The latter is given by Crank (1975):

$$(c-c_1)/(c_0-c_1)=1+(2a/\pi r)_{n=1}^{4}\,'\,((-1)^n/n)\sin((n\pi r)/a)\exp((-Dn^2\pi^2t)/a^2)$$

where c=concentration, c_1=original concentration, c_0=concentration at the surface of the crystal, a=radius of crystal, r=distance to which diffusion has penetrated measured from the center of crystal, D=diffusion coefficient, and t=time in seconds. Graphical solutions for this equation in terms of $(c-c_1)/(c_0-c_1)$, r/a, and Dt/a^2 are given by Crank (1975).

For both xenocrysts, a is the distance from the center of the crystal to the innermost part of the rim where $c_0=Fo_{76}$. For crystal 1, a=0.24mm whereas for crystal 2 a=0.17mm. Assuming that diffusion has just reached the center of the crystal (as suggested by the zoning patterns), then r/a=0 and $(c-c_1)/(c_0-c_1)=0$. The diffusion coefficient for Mg_{90}-Fe_{10} diffusion in olivine can be

calculated using data given by Barton and Wyers (1991), and is $5.09*10^{-11}$ cm^2 sec^{-1} at a temperature of 1020°C (1293K). This temperature is that calculated for equilibration of the phenocrysts in SI173 by Barton (personal communication, 1999).

Using the data given above, reequilibration times for the olivine xenocrysts described in this study are 4.6 days for crystal 1 and 2.3 days for crystal 2. These are the times required for partial reequilibration of the olivines with the hybrid magma, and therefore represent residence times of the olivine xenocrysts in the hybrid magma. The residence times provide a quantitative estimate of the time that elapsed - 2-5 days - between mixing and eruption. These times are relatively short, confirming the conclusion reached by previous workers (eg. Wyers and Barton, 1986) that magma mixing triggers volcanic eruptions.

Acknowledgements

I would like to thank Dr. Barton for all his patience, hard work and laughter. Mike Commerford for his patience and guidance while I worked on the probe, and thanks to Karen Tefend for siting with me and helping me along the way. To Eric, thanks for putting up with me during the whole process.

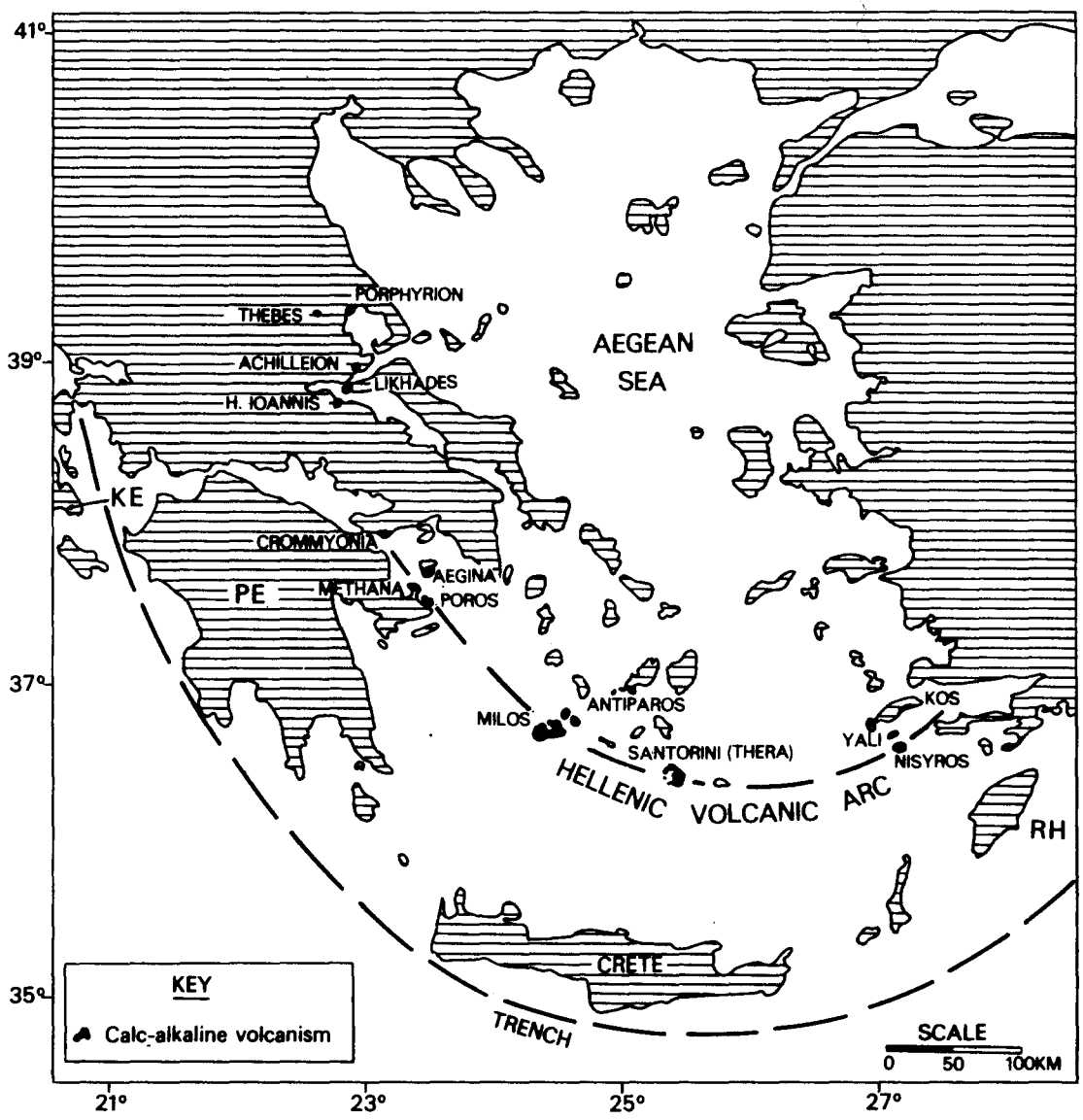

Figure 1. Map of Agean Sea. (Huijsmans, 1985)

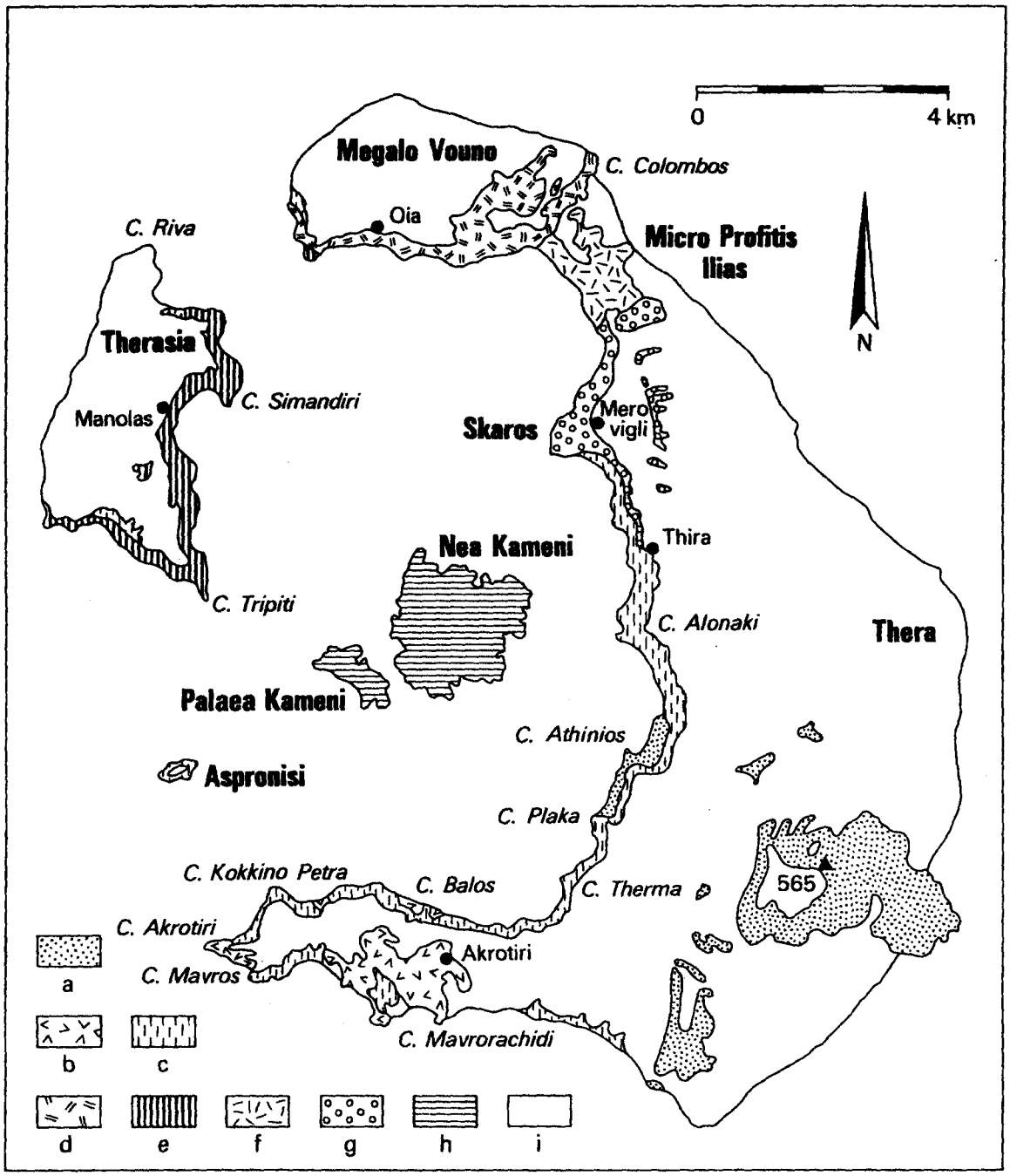

Figure 2. Geological map of Santorini showing the different eruption centers. a=prevolcanic basement; b=Akrotiri volcanoes; c=Thera volcano; d=Megalo Vouno complex; e=Therasia volcanoes; f=Micro Profitis Ilias; g=Skaros volcano; h= post-caldera lavas of Kamenis; I=Minoan deposits (Huijsmans and Barton, 1989)

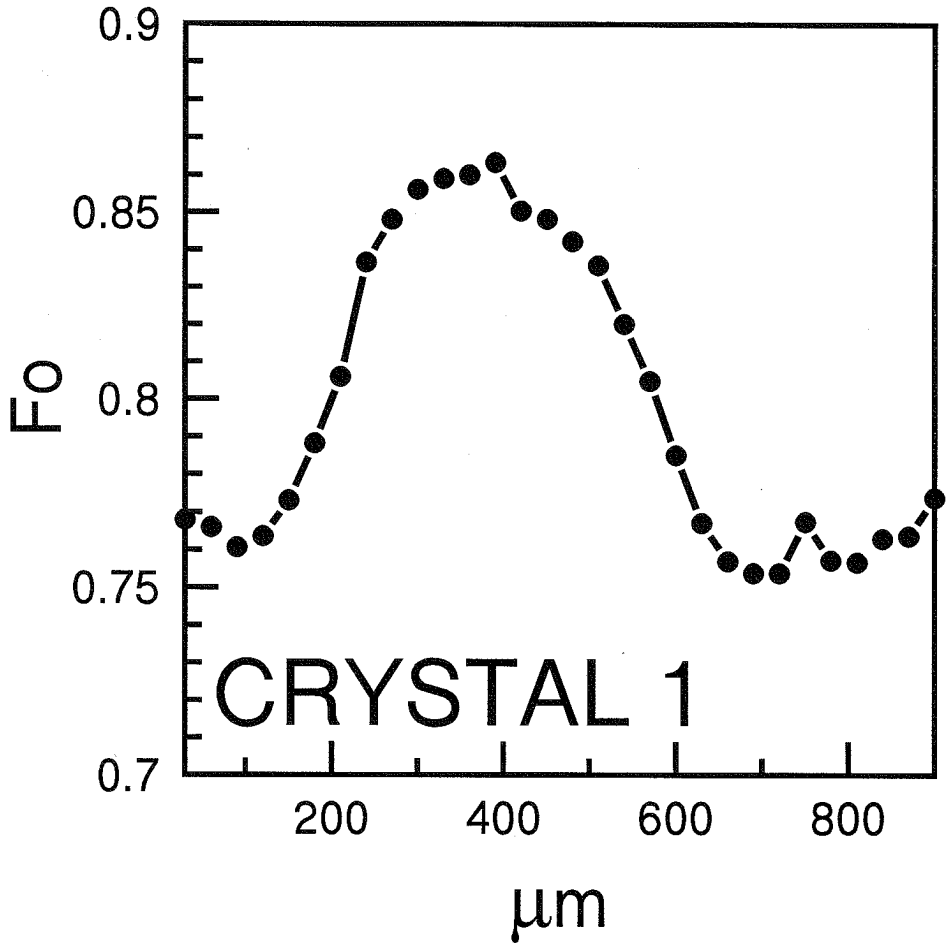

Figure 3. Concentration of forsterite vs. diameter of crystal 1

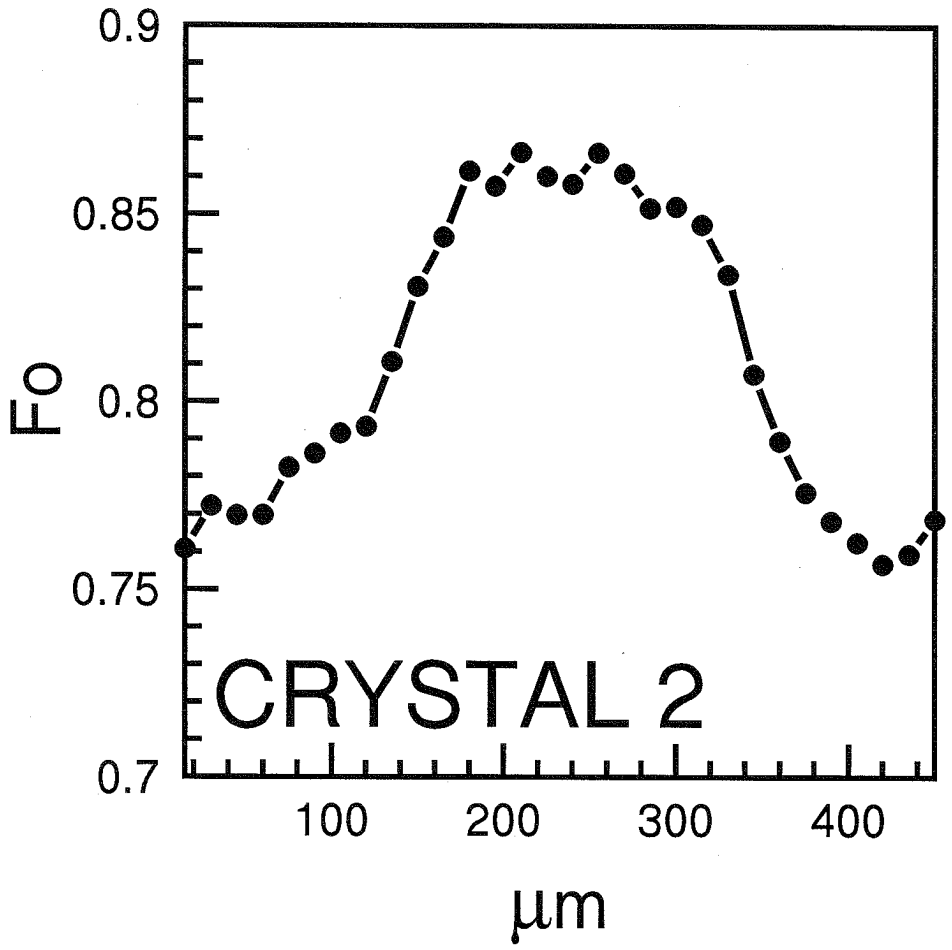

Figure 4. Concentration of forsterite vs. the diameter of crystal 2

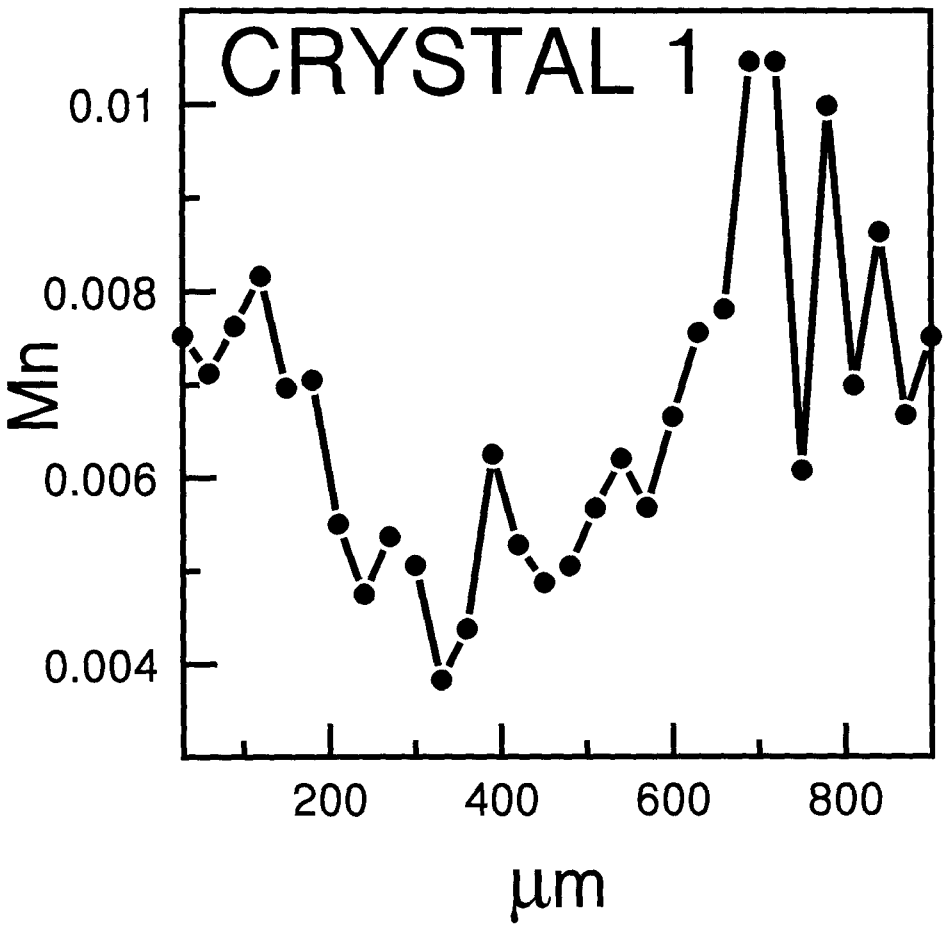

Figure 5. Manganese vs. the diameter of crystal 1.

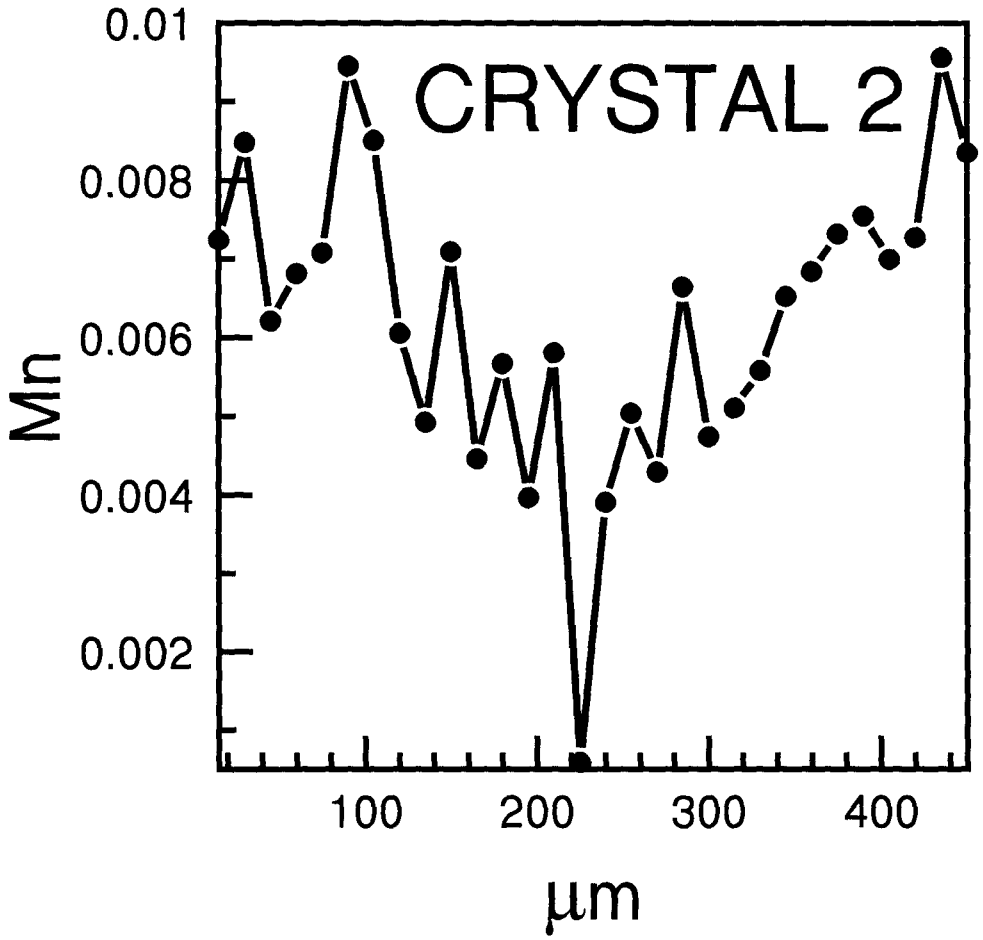

Figure 6. Manganese vs. the diameter of crystal 2.

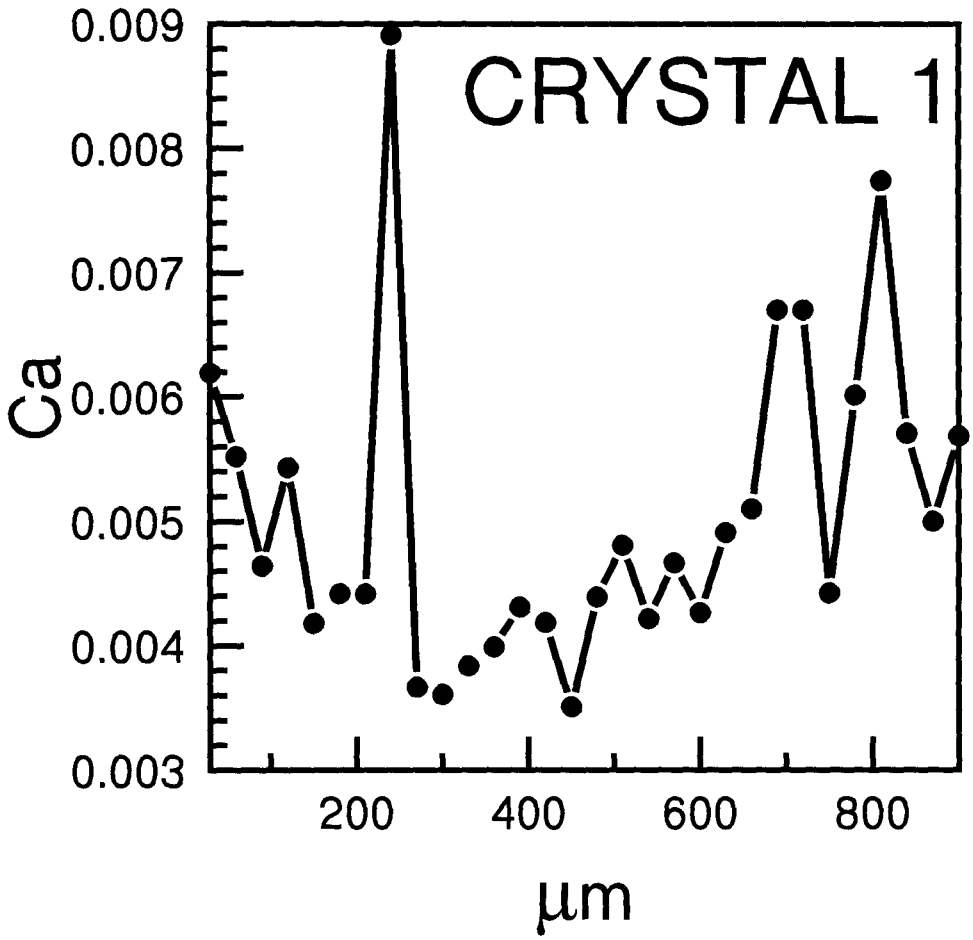

Figure 7. Calcium vs. the diameter of crystal 1.

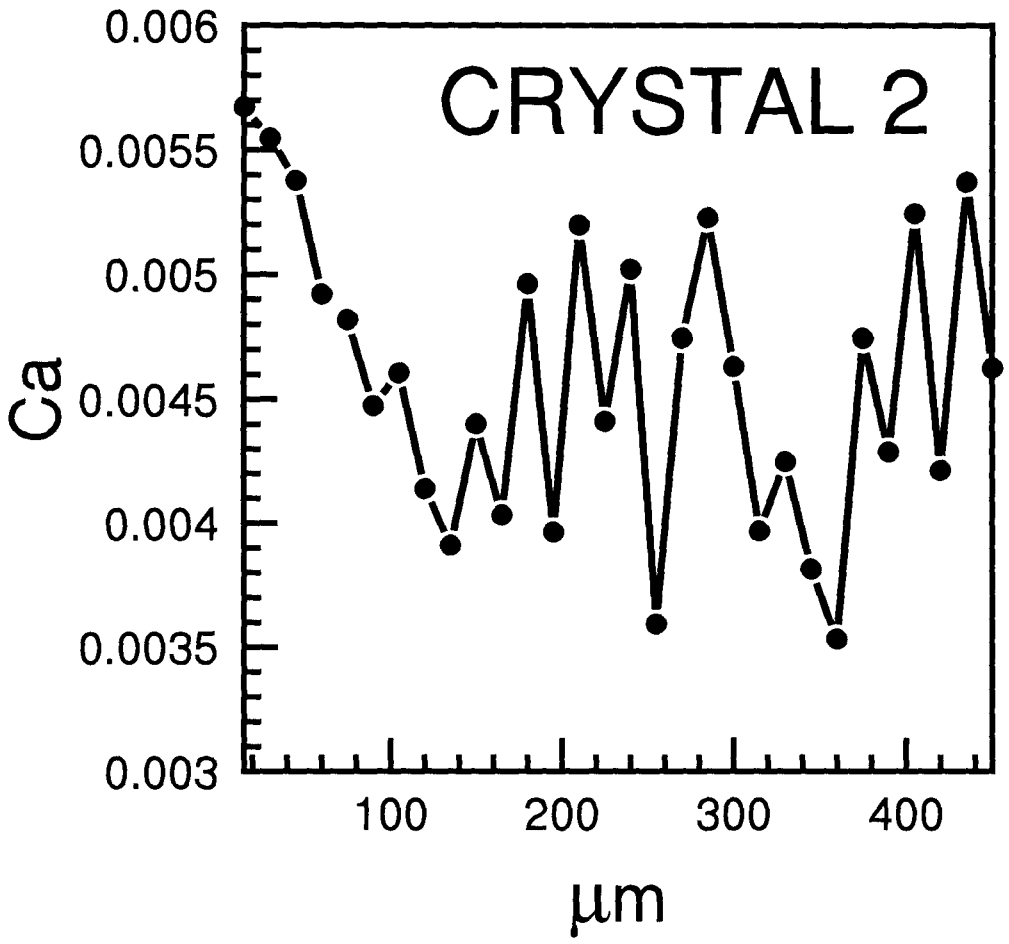

Figure 8. Calcium vs. the diameter of crystal 2.

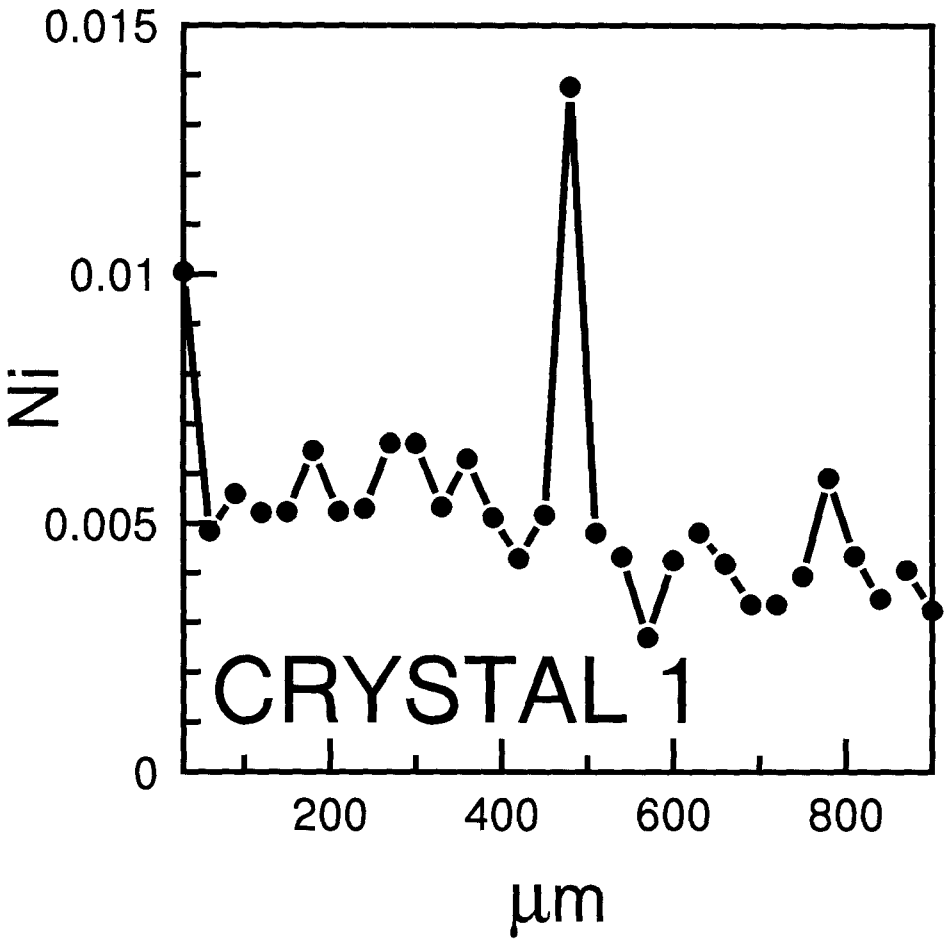

Figure 9. Nickel vs. the diameter of crystal 1.

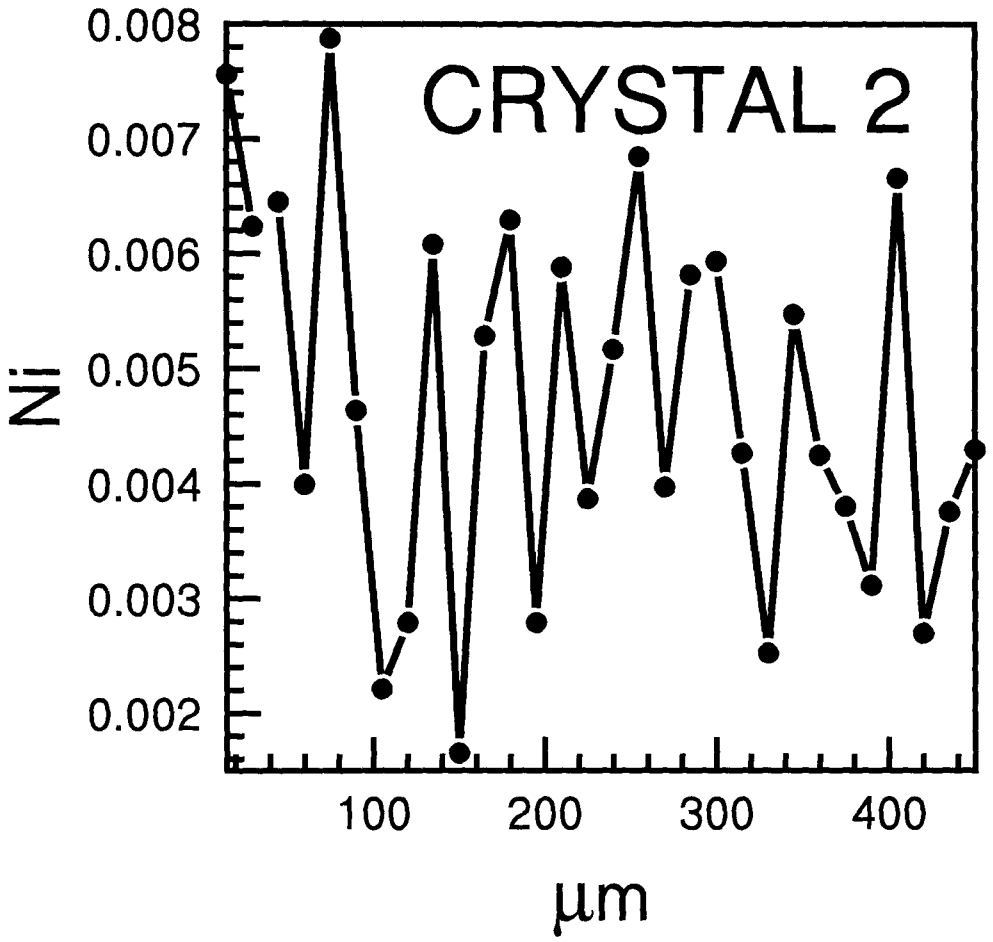

Figure 10. Nickel vs. the diameter of crystal 2.

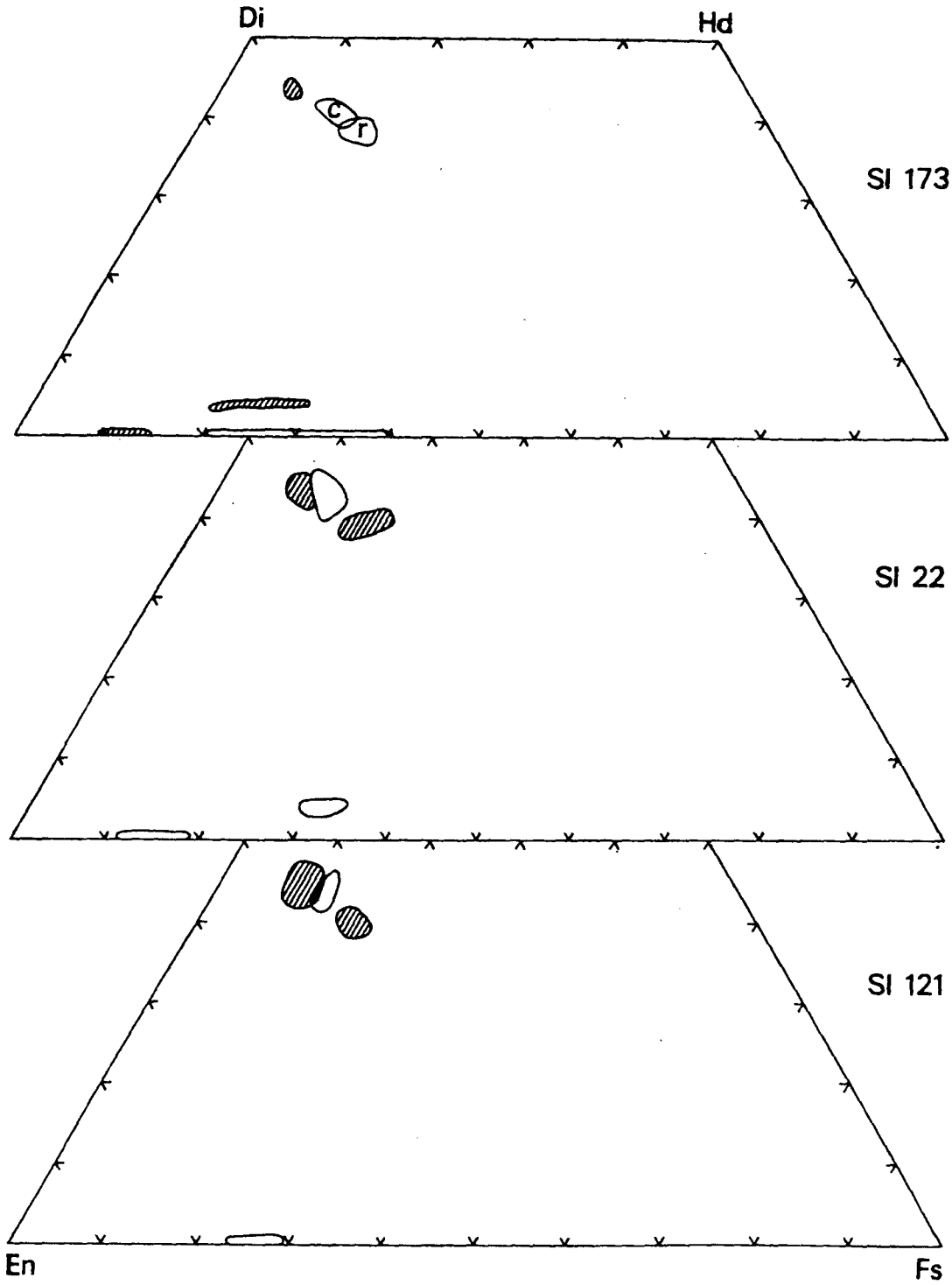

Figure 11. Mineralogy of olivine, clinopyroxene, and orthopyroxene in the samples SI173, SI122, SI121. SI173: shading = basic xenocrysts, c=core, r= rim; SI122 and SI121 clinopyroxene: shading = core compositions, open = rim composition. (Huijsmans 1985)

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